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# Investigating Conductivity to Predict Magnesium Addition Requirements for Struvite Precipitation in Swine Manure Slurries

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**Abstract.** *The goal of this project was to develop a system that identified magnesium demand for struvite formation by monitoring conductivity changes during continuous injection of magnesium chloride in several swine manure slurries. The conductivity of six manure slurries was monitored to identify the response due to magnesium chloride injection ($MgCl_2$) and struvite precipitation. Struvite precipitation is a technically feasible treatment method for phosphorus removal and recovery from manure slurries (Burns et al., 2003; Bowers and Westerman, 2005a). Swine manure slurries often require the addition of magnesium ($Mg^{2+}$) to force struvite precipitation. The quantity of $Mg^{2+}$ required for maximized phosphorus removal can be determined through laboratory tests. Optimized struvite precipitation in a field setting requires a real-time method to determine $Mg^{2+}$ addition rates during a land application event. This article discusses the requirements of an automated control system which monitors and controls the injection of $Mg^{2+}$ to force struvite precipitation, accounting for real-time variations of magnesium demand. Theoretical predictions and pure solution tests provided information capable of determining the magnesium demand for struvite precipitations. After testing six different manures in triplicate, the conductivity responses did not follow theoretical predictions and failed to provide any indication of optimum magnesium injection rates for phosphorus removal.*

**Keywords.** *Manure, Phosphorus, Struvite, Magnesium Chloride, Conductivity.*

Struvite is a crystalline precipitate technically described as magnesium ammonia phosphate hexahydrate ($MgNH_4PO_4*6H_2O$). To form struvite, magnesium, ammonia, and phosphate must be available in an ionic form to provide an adequate precipitation potential. Magnesium is the limiting ion in typical manure slurries, meaning that its addition can promote struvite formation. In a pure solution, a 1:1:1 ($Mg^{2+}$:$NH_4^+$:$PO_4^{3-}$) molar ratio will form struvite. In complex organic solutions, such as manures, this ratio may not be adequate, requiring higher than stoichiometric magnesium additions to overcome complexing reactions (Burns et al., 2003). The objective of this project was to develop a real-time magnesium requirement estimate based on conductivity measurements.

Determining appropriate magnesium injection rates is paramount to optimize struvite precipitation. Phosphate variability within and across manure slurries requires variable amounts of magnesium injection and pH amendment. Furthermore, the stratified nature of most manure slurry storages means that manure slurry composition is highly variable during land application events. Current methods used to determine magnesium demand rely upon initial analysis of manure slurries which do not account for compositional variations during land application. A feasible farm-scale system should be capable of determining the real-time magnesium amendment rates under variable conditions with robust equipment for a reasonable initial investment.

The development of an automated feedback control system for magnesium amendment would allow a struvite reactor to account for variations within manure slurries and across different manure handling systems. A flow injection analysis (FIA) approach may provide information that allows for the determination of the struvite precipitation potential and degree of constituent ion availability for further struvite formation. Ion selective electrodes (ISE) are essential items of FIA systems and can be used to directly monitor analyte ion activities or to monitor the activities of reagent ions after reaction with analytes (Coetzee and Gardner, 1986). Monitoring $Mg^{2+}$, $NH_4^+$, or $PO_4^{3-}$ ion activity with an ISE would allow for direct measurement of the struvite reaction. Speciation modeling with MINTEQ (Battelle Pacific North Western Laboratory, PNL) indicates that a magnesium ISE could be used to infer completion of struvite precipitation (Ali et al., 2003).

Magnesium ISE sensors can be found for applications in molten metal processing (Fergus, 2000) and for biological

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fluids such as blood (Gunzel and Schlue, 2002). However, no appropriate magnesium-specific ISEs are available for application in manure systems. Ammonia and ammonium ISEs are commercially available (*Thermo Electron*, Waltham, Mass.) and have been thoroughly investigated. Problems with fouling and drift in manure solutions decrease the reliability of using ammonia ISE to monitor the struvite reaction in manure slurries (Winkler et al., 2004). Also, the solubility of ammonia and ammonium is dependant on solution pH. The ideal pH for struvite precipitation is 8.5-9.0; at this point the concentration of ammonium is highly sensitive to changes in solution pH. A change in solution pH will affect the ISE output, and may provide inaccurate information pertaining to the struvite reaction. Phosphate ISEs have been implemented to monitor soil macronutrients in real-time (Kim, 2006), however literature and product searches did not find a wastewater application of phosphate ISE's.

## Theory

Monitoring conductivity in a solution during struvite reaction could provide information indicating reaction completion and magnesium demand. Specific conductance, K (S/cm), commonly used to determine the total dissolved solid content of a solution, is a direct measure of ions in solution. It is generally referred to as conductivity, and varies with the type and number of ions in solution. As struvite precipitates out of solution, conductivity will change dependant upon the amendment procedure and reaction state. Specific conductivity, κ, can be calculated from the following fundamental relationship shown in equation 1.

$$\kappa = \frac{\Lambda \times N}{1000} \tag{1}$$

where
$N$ = normality of the solution (eq/L)
$\Lambda$ = equivalent conductance of the solution (S $m^2$/mol)

Molar (equivalent) conductance of the solution at infinite dilution, $\Lambda_0$, is calculated by the summation of the equivalent ionic conductivity of each species in solution, $\lambda_o$ (eq. 2). Table 1 provides a list of molar (equivalent) ionic conductivities at infinite dilution for species of interest in this system.

$$\Lambda_0 = \lambda_0^{+} + \lambda_0^{-} \tag{2}$$

For a simple system, the addition of $MgCl_2$ in distilled water will have the predicted conductivity shown in equation 3.

**Table 1. Molar (equivalent) conductivity, $\lambda_o$ (Infinite Dilution at 25°C) for participating ions in struvite precipitation *CRC Handbook of Chemistry and Physics*, 88th ed. (2008).**

| Ion | | $\lambda_o$ ($10^{-4}$ S $m^2$/mol) |
|---|---|---|
| Phosphate | 1/3 $PO_4^{3-}$ | 92.8 |
| Ammonium | $NH_4^+$ | 73.5 |
| Magnesium | 1/2 $Mg^{2+}$ | 53.0 |
| Chlorite | $Cl^-$ | 76.3 |
| Sodium | $Na^+$ | 50.1 |
| Hydroxide | $OH^-$ | 198 |
| Hydrogen | $H^+$ | 349.6 |

$$\kappa = \left[Mg^{2+}\right]\lambda_0^{Mg2+} + \left[Cl^-\right]\lambda_0^{Cl-} \tag{3}$$

For a more complex system, where multiple species are present, the relationship shown in equation 3 expands to include all ionic species in solution. As magnesium chloride is added to a solution with available phosphate and ammonium, struvite may precipitate. As $MgCl_2$ is added to a slurry, we hypothesized that the rate of change of conductivity would depend on whether or not struvite was precipitating. Specifically, when struvite is precipitating, several ions would be removed from solution (phosphate, ammonium, and magnesium) while the chloride ions would be added to solution, creating a constant decrease in conductivity. And, when struvite precipitation ceases, an inflection point would mark a change to an increasing slope as additional $MgCl_2$ is added but not utilized in the struvite reaction. Mathematical comparison methods, such as extrapolation, of these two hypothesized slopes and inflection point identification may provide an estimate of struvite formation completion.

To provide proof of concept, equation 4 was used to model struvite precipitation in pure solution. For simplicity, this model assumed that a $Mg^{2+}$ dose equal to the molar concentration of $PO_4^{3-}$ in solution produces only struvite, and removes all of the $PO_4^{3-}$. Furthermore, this model does not account for changes in pH due to forced struvite reaction or other environmental factors, the effect of concentration on the activity of specific ions, the decomposition or establishment of magnesium or other constituent ion complexes, and that no side reactions are occurring, such as with calcium compounds. In actual situations, the degree of phosphate removal via struvite precipitation is dependant upon the conditional solubility product of struvite and will not be 100% efficient. Based on our working hypothesis, monitoring the rate of conductivity change during constant-rate magnesium chloride injection may allow detection of struvite formation process completion, thus indicating a point of struvite saturation regardless of actual solute concentrations, ion availability and activity, or pH.

$$\begin{aligned}\kappa = {} & \left[Mg^{2+}\right]\lambda_0^{Mg^{2+}} + \left[Cl^-\right]\lambda_0^{Cl^-} \\ & + \left[PO_4^{3-}\right]\lambda_0^{PO_4^{3-}} + \left[NH_4^{+}\right]\lambda_0^{NH4^{+}}\end{aligned} \tag{4}$$

# Materials and Methods

Three experiments were performed to validate the theoretical predictions of conductivity response to magnesium amendment in pure solutions. One experiment was designed to determine the applicability of conductivity response in swine manure slurries. All experiments used well-mixed 1.5-L sample volumes in 2.5-L Nalgene beakers. Conductivity and pH were logged every 5 seconds using an Orion 4-Star pH/Conductivity probe (Thermo Electron, Waltham, Mass.) connected to a laptop computer. Laboratory grade magnesium chloride ($MgCl_2$) was selected as a magnesium source due to its high solubility. Magnesium chloride was prepared to specific concentrations based on the testing protocol and was added continuously to the sample by a Masterflex peristaltic pump (Cole-Parmer, Vernon Hills, Ill.). Figure 1 shows the experimental setup for monitoring the conductivity of solutions during $MgCl_2$ injection.

### Magnesium Chloride Injection in Distilled Water

To ensure that the conductivity meter was responding as theoretically predicted, the conductivity change in distilled water due to $MgCl_2$ amendment was evaluated. In this experiment, 0.05 molar $MgCl_2$ was continuously injected at a flow rate of 13 mL/min into 1.5 L of distilled water at 24°C for 7 min; conductivity and pH were monitored continuously for the duration of the experiment.

### Magnesium Chloride Injection in $PO_4^{3-}$:$NH_4^+$ Solution

Four pure 1.5-L samples of ammonia phosphate were made to simulate the basic struvite reaction. Prior to magnesium injection, the pH of the solution was raised to 8.5 with sodium hydroxide. The solution was continuously stirred at 24°C and a 5-min reaction time was allowed between doses. Conductivity and pH were monitored while magnesium was dosed from 10% to 130% of the phosphate stoichiometric requirement at 400, 600, 800, 1000 mg/L $PO_4^{3-}$. A model of the simplified struvite reaction conductivity response was calculated from equation 4 using the molar conductivities and the concentrations of constituent ions $PO_4^{3-}$, $NH_4^+$, $Mg^{2+}$, and $Cl^-$. Equation 4 was solved at several points throughout the reaction, accounting for undersaturated and oversaturated struvite precipitation conditions.

### Magnesium Chloride Injection in Manure

Swine manure slurry samples were collected during custom field application events in the spring of 2006 from six Iowa swine production facilities. Samples were stored in 5-gal sealed plastic buckets at 4°C. Each sample was analyzed at 25°C in triplicate for dissolved reactive phosphorus ($PO_4^{3-}$), ammonia ($NH_3$), and total solids (TS). Dissolved reactive phosphorus concentration was analyzed using Standard Method 4500-P E (APHA, 1998). Ammonia concentration was analyzed using Standard Method 4500-$NH_3$ B & C for (APHA, 1998). Total solids concentrations was analyzed using Standard Method 2540 B (APHA, 1998). Table 2 provides a description of the facility operation and sampling information including animal type, manure storage system, and the time the sample was collected during pump-out.

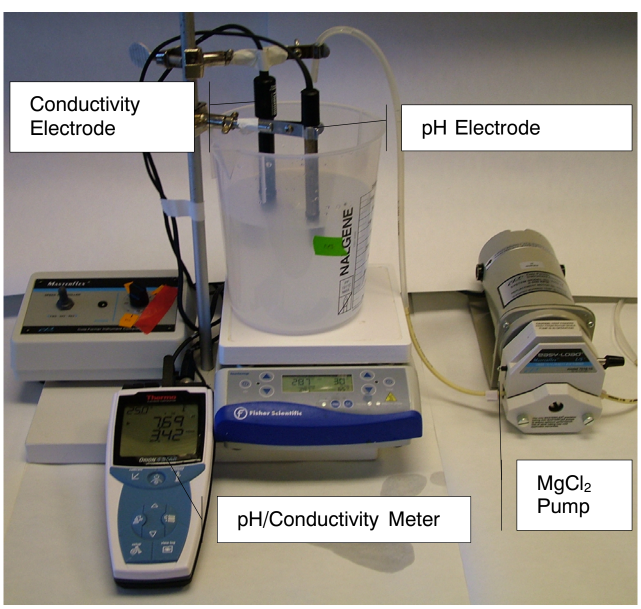



**Figure 1. Experimental set up of magnesium injection and conductivity monitoring system.**

**Table 2. Facility information of swine manure slurry sources and sampling time.**

| Sample | Storage | Pump-out Stage |
|---|---|---|
| Finisher[a] 1 | Lagoon[b] | End[c] |
| Finisher 2 | Holding tank[d] | Prior to agitation[e] |
| Finisher 3 | Lagoon | Middle[f] |
| Finisher 4 | Deep pit[g] | Top[h] |
| Farrowing[i] 1 | Deep pit | Middle |
| Farrowing 2 | Deep pit | End |

[a] Finisher: Designates manure slurry was collected from a swine finishing facility.
[b] Lagoon: Manure slurry was collected from an uncovered lagoon storage system.
[c] End: Indicates that the manure slurry sample was collected at the end of the pump-out event near the bottom of the storage system.
[d] Holding tank: Manure slurry was collected from an uncovered concrete storage tank.
[e] Prior to agitation: Indicates that the manure slurry sample was collected prior to agitation of the stored manure slurry.
[f] Middle: Indicates that the manure slurry sample was collected halfway through the pump-out event with approximately half of the stored manure slurry remaining.
[g] Deep pit: Manure slurry was collected from an under-floor deep pit storage system.
[h] Top: Indicates that the manure slurry sample was collected shortly after pump-out was initiated from an agitated manure slurry.
[i] Farrowing: Designates manure slurry was collected from a swine farrowing facility.

Table 3 identifies the physical and chemical results from analysis of swine manure samples used in this study. Time to saturation, $T_{sat}$, identifies the $MgCl_2$ pump time required to achieve a 1:1 stoichiometric ratio based on initial phosphate concentration. $T_{sat}$ was used to maintain a relatively equal magnesium injection rate between manures and varied depending on the manure characteristics; triplicate manure samples used a fixed $T_{sat}$. Note that samples Finisher 4 and Farrowing 2 did not maintain a stable reading for the duration of the test, this is attributed to large suspended particles bridging on the conductivity probe; no further testing was performed on these samples. Conductivity and pH for each manure sample was monitored until 250% of the initial stoichiometric phosphate requirements had been applied (2.5 × $T_{sat}$).

To identify the point when struvite precipitation was maximized, a second test on sample Finisher 4 was performed. This experiment monitored the conductivity and pH as described previously. However, the amount of magnesium injection time was increased to approximately 700% of the initial stoichiometric phosphate requirements (7 × $T_{sat}$). Triplicate 30-mL samples were extracted prior to pH adjustment, after pH adjustment, every 2 min for the duration magnesium injection, and after magnesium injection was complete for dissolved reactive phosphorus (DRP) analysis.

**Table 3. Dissolved reactive phosphorus (DRP) mg/L as $PO_4{}^{3-}$, percent total solids (TS), ammonia ($NH_3$) mg/L and magnesium injection time to saturation ($T_{sat}$) for each manure slurry tested.**

| Sample | DRP (mg $PO_4{}^{3-}$ /L) | TS (%) | $NH_3$ (mg/L) | $T_{sat}$, (min) |
|---|---|---|---|---|
| Finisher[a] 1 | 130 | 4.7 | 1800 | 4.5 |
| Finisher 2 | 620 | 4.6 | 4600 | 5.0 |
| Finisher 3 | 500 | 1.4 | 2300 | 4.1 |
| Finisher 4 | 950 | 6.4 | 4400 | [c] |
| Farrowing[b] 1 | 390 | 2.4 | 2900 | 4.7 |
| Farrowing 2 | 390 | 8.0 | NA | [c] |

[a] Finisher: Designates manure slurry was collected from a swine finishing facility.
[b] Farrowing: Designates manure slurry was collected from a swine farrowing facility.
[c] No stable conductivity reading.

## Results and Discussion

### Magnesium Chloride Injection in Distilled Water

Experimental measurements obtained were plotted with theoretical conductivity predictions at equal concentrations. Figure 2 shows the comparison of the experimental and theoretical results. This plot shows that the experimental data is in agreement with the theoretical calculations of conductivity.

### Magnesium Chloride Injection in $PO_4{}^{3-}$:$NH_4{}^{+}$ Solution

Figure 3 presents the experimental and theoretical curves of $MgCl_2$ injection into 1000 mg/L $NH_4H_2PO_4$ solution. Based on the theoretical model, as struvite is formed phosphate, ammonium, and magnesium are removed from solution while chloride is added. The change in conductivity

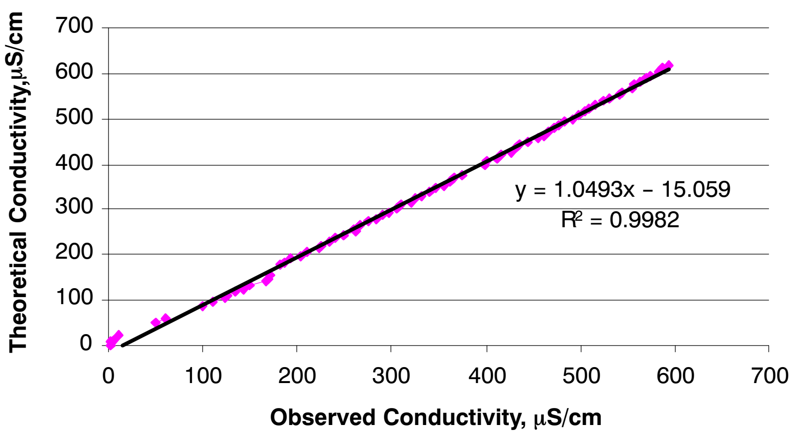



**Figure 2. Comparison of theoretical model and experimental conductivity response to magnesium chloride injection in distilled water.**

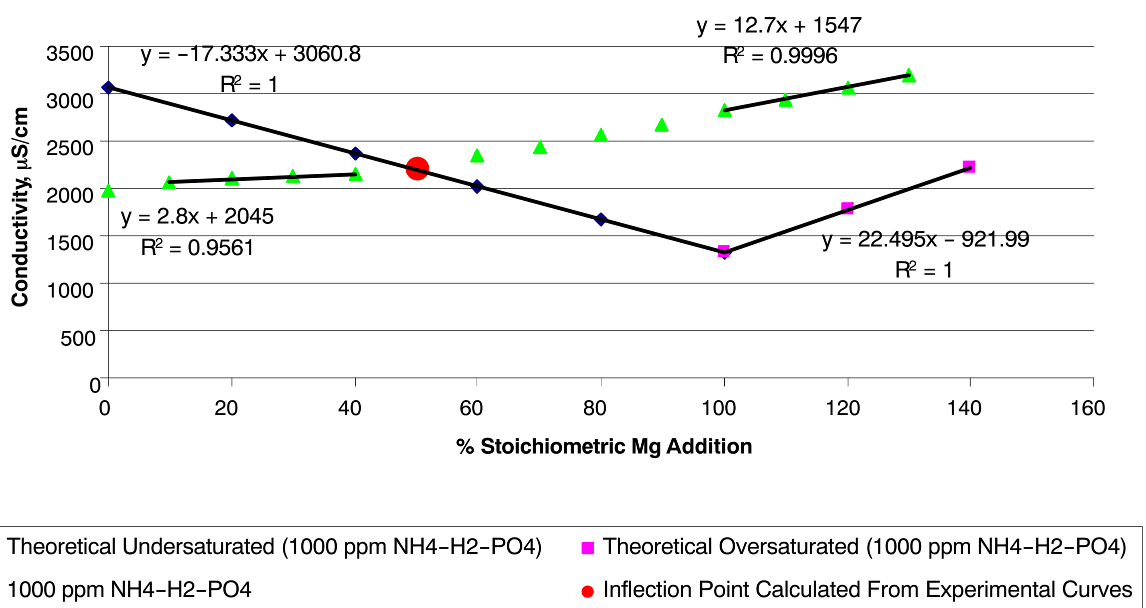



**Figure 3. Theoretical model and experimental conductivity response to magnesium chloride addition in 1000 ppm $PO_4{}^{3-}$-$NH_4{}^{+}$ solution. The inflection point of conductivity in the theoretical model represents magnesium saturation and completed struvite formation; this inflection point is also seen in the experimental data from pure solutions.**

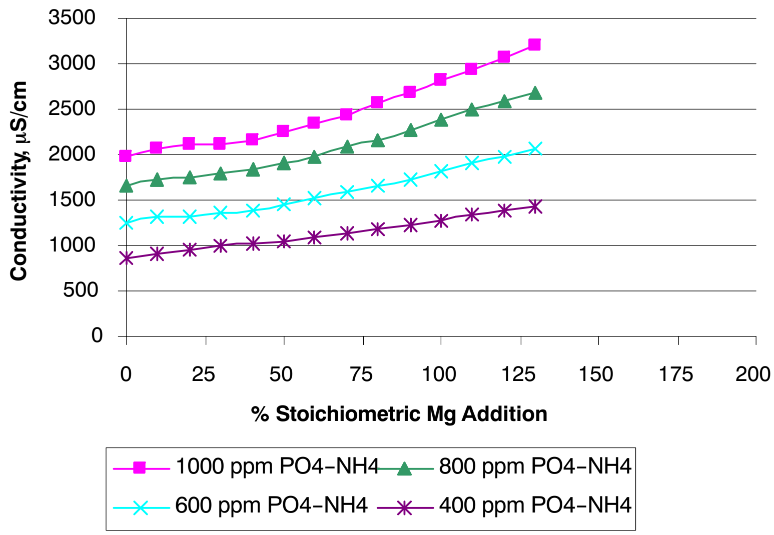



**Figure 4. Experimental conductivity response to magnesium chloride addition in multiple $PO_4{}^{3-}$-$NH_4{}^{+}$ solutions.**

is negative and linear during this portion of the reaction. When phosphate or ammonia becomes limiting, struvite no longer precipitates; with continued injection of magnesium chloride, both magnesium and chloride ions enter solution while no ionic removal occurs. The change in conductivity then provides a slope which is positive and linear. The change in the conductivity slope could be used to identify magnesium saturation and optimized struvite formation. Extrapolation of the assumed undersaturated and oversaturated struvite conductivity response curves from the experimental solution provides an inflection point that corresponds with magnesium saturation at approximately 50% of the stoichiometric magnesium addition, with a slope 4.5 times higher in oversaturated conditions.

Figure 4 presents the experimental conductivity response curves of $MgCl_2$ injection into multiple $PO_4{}^{3-}$:$NH^{4+}$ solutions. Using linear regression lines similar to those in figure 3, each experimental conductivity response curve was investigated to determine an approximate inflection point to identify magnesium demand for struvite precipitation. Through data analysis it was determined that an inflection point occurred at approximately 50%, 50%, 45%, and 58% of the stoichiometric magnesium demand in 1000, 800, 600, and 400 mg/L $PO_4{}^{3-}$:$NH^{4+}$ solutions, respectively. The inflection points were identified by slope changes within each data set.

### Magnesium Chloride Injection in Manure Slurries

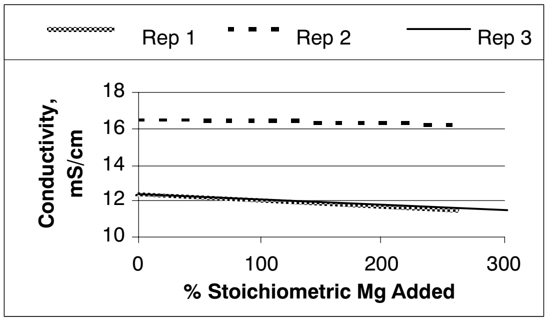
To determine if this process was applicable over a broad range of operating systems, several manures were collected from other swine farms (as listed in table 2). Triplicate experiments were used to develop conductivity curves for these manures. Figures 5(a-d) illustrate the conductivity response curves from the four swine facilities, an inflection point indicating magnesium demand for struvite precipitation was not observed; furthermore, all manures provided a negative slope contradictory to theoretical predictions. Based on this information, it would not be possible to determine the magnesium demand by monitoring conductivity.

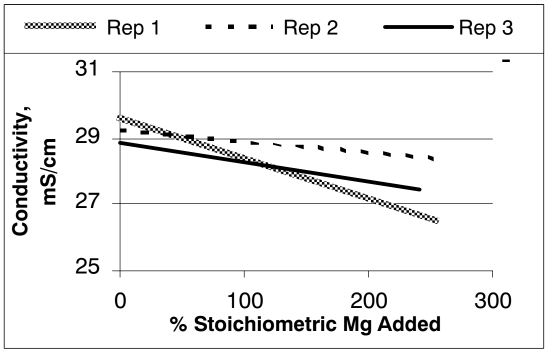
To identify the exact point of phosphate removal, tests were performed on Finisher 3 over an increased magnesium injection amount. Finisher 3 was selected because it provided a conductivity response curve with the greatest stability. Excess magnesium was added to ensure that maximum phosphate removal occurred. Samples were recovered throughout the experiment for DRP analysis. Figure 6 provides the extended conductivity response curve and the corresponding DRP removal value for magnesium injection into manure slurry from Finisher 3.

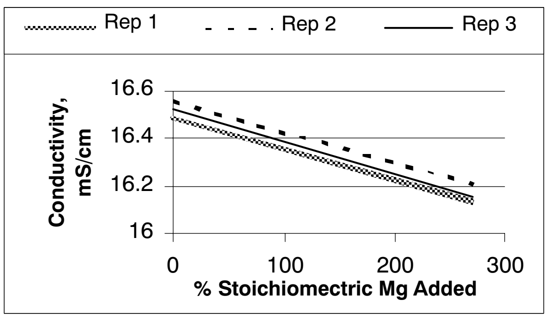
The phosphate analysis indicated that approximately 88% of the available dissolved reactive phosphorus (DRP) was removed during pH adjustment. The initial pH of 6.85 was adjusted to 8.48 with sodium hydroxide prior to magnesium amendment. The reduction of DRP prior to magnesium injection can most likely be attributed to precipitation of struvite with magnesium initially present in the manure sample and complexing of DRP with other metal ions such as calcium. The extended magnesium injection failed to produce an inflection point indicating magnesium saturation and optimized struvite precipitation. The lack of an inflection point indicates that when magnesium chloride is added in excess of phosphate requirements it may continue to complex with ions in the solution, reducing the specific conductance of the solution. Furthermore, $MgCl_2$ is acidic and amendment lowers the pH of the solution. For optimized struvite precipitation, pH is usually monitored and controlled, however this process may have a significant impact on hydrogen, hydroxide, and/or bicarbonate concentrations, and may force other non-struvite related complexes to form or dissociate, offsetting or obscuring any visible conductivity changes directly related to struvite precipitation.

## Conclusion

The goal of these experiments was to develop a system that identified magnesium demand for struvite formation by monitoring conductivity changes during continuous injection of $MgCl_2$ into manure slurries. Theoretical predictions and pure solution tests provided information capable of determining the magnesium demand for struvite precipitations. After testing six different manures in triplicate, the conductivity responses did not follow theoretical predictions and failed to provide any indication of



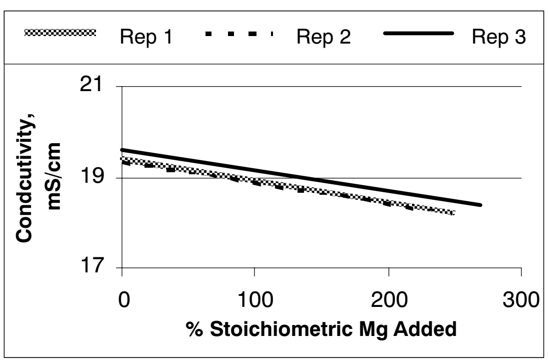




**Figure 5. Conductivity response to magnesium chloride injection in manure slurries collected from multiple Iowa swine production facilities. No conductivity inflection point indicating magnesium saturation or completed struvite formation was identified.**

optimum magnesium injection rates for phosphorus removal. We hypothesize that side reactions, such as those associated with formation of calcium phosphates, may be responsible for this failure, or that changes in solution pH create substantial changes in ion concentrations which offset or obscure any visible conductivity changes directly related to struvite precipitation. The conductivity response curves generated from the manure samples have a generally stable

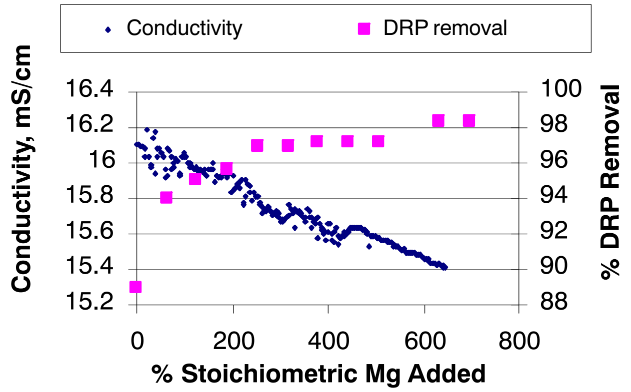



**Figure 6. Conductivity response and dissolved reactive phosphorus (DRP) removal with magnesium chloride addition in manure slurry from Finisher 3: collected from a lagoon storage system of a swine finishing facility half-way through pump-out.**

and negative slope and do not identify a magnesium saturation point.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